

# Portable Sensor for Hazardous Waste

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## Introduction

Physical Sciences Inc. (PSI) has just completed the second phase of a 5-year program to develop a portable monitor for sensitive hazardous waste detection.<sup>1</sup> The current goal of the program is to develop our concept to the prototype instrument level and to thoroughly test it in the field. Our monitor is a compact, portable instrument that allows real-time, *in situ*, monitoring of hazardous wastes, principally RCRA heavy metals (Pb, Cd, Cr, Sb, As, Hg, and Be) and radionuclides (U, Th, Tc). This instrument should prove useful in a variety of commercial and DOE applications (please see Figure 1) such as site screening, clean-up process control, health monitoring, and continuous emission monitoring of stack gases from power plants, incinerators and thermal waste treatment facilities.

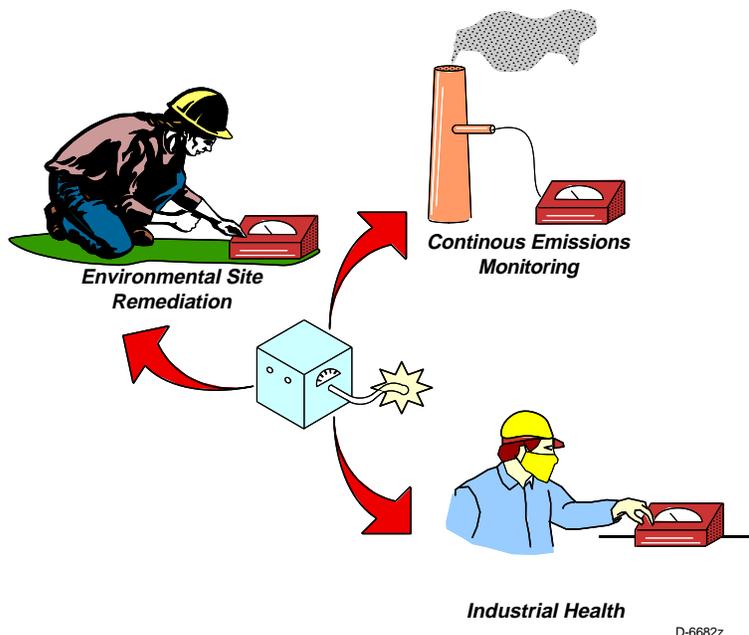


Figure 1. Potential applications for hazardous waste monitor.

Our approach is to excite atomic fluorescence by the technique of Spark-Induced Breakdown Spectroscopy (SIBS). This system vaporizes particulate samples in a high energy, electrically generated spark. With suitable processing of the fluorescence radiation, background emissions can be suppressed with respect to the atomic fluorescence of the analyte species.

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Each element in the excitation region has a unique spectroscopic signature which allows it to be distinguished from emissions from other species in the discharge region. The overall intensity of the emission from each element provides a quantitative measure of the amount of the element in the sample.

The program's second phase had three primary components:

- Technology extension
  - demonstrate sensitive detection of heavy metals and radionuclides
  - develop an aerosol generator for precise calibrations
- Application identification
  - survey D&D user needs
- Engineering design of prototype instrument.

During the program's third phase, we will fabricate the prototype and field test it at a number of sites, including several of DOE's Large Scale Demonstration Projects (LSDPs). We began this process recently by demonstrating our technology in a test of continuous emissions monitoring (CEM) technologies, sponsored jointly by the Environmental Protection Agency (EPA) and the Department of Energy's Mixed Waste Focus Area (MWFA), at EPA's rotary cement kiln simulator at Research Triangle Park.

The following sections describe our technology in more detail and discuss the prototype engineering design.

### Spark-Induced Breakdown Spectroscopy (SIBS)

As previously mentioned, our technology uses atomic fluorescence emission for monitoring the hazardous wastes. We excite this fluorescence by the technique of Spark-Induced Breakdown Spectroscopy (SIBS). This approach, illustrated schematically in Figure 2, uses a high energy, electrically generated spark to create a plasma at temperatures of 10,000 to 20,000 K. At these temperatures, any particles initially within the plasma volume are completely vaporized and all molecular species are fully atomized. In addition, the high plasma temperatures excite a substantial fraction of atoms in the volume to high energy electronic states. It is the

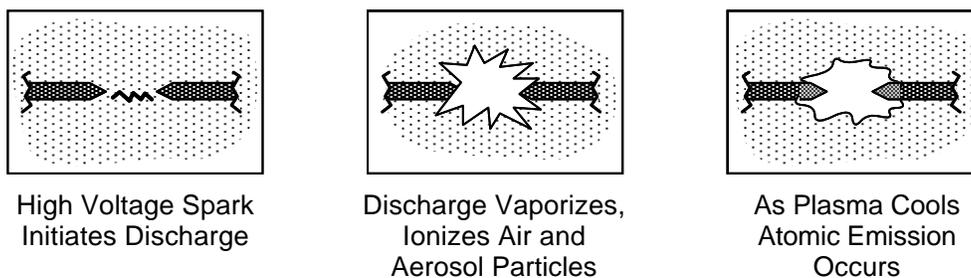


Figure 2. Schematic representation of Spark-Induced Breakdown Spectroscopy (SIBS).

subsequent fluorescence from these states which provides the monitoring diagnostic. Each element in the excitation region has a unique spectroscopic signature which allows it to be distinguished from emissions from other species in the discharge region. The overall intensity of emission from each element provides a quantitative measure of its abundance in the sample. This approach provides highly sensitive detection of species in liquid and solid aerosols as well as those initially in the gas phase.

Spark spectroscopy itself is a relatively old and established approach to metals analysis. We have, however, developed an enhanced approach to the practice of spark spectroscopy which enables our SIBS instruments to make sensitive, quantitative measurements.

Our approach employs a spark in air between two electrodes of a proprietary design. Further, we use carefully tailored data processing to enhance spectral emissions from the analyte species with respect to background emissions. This process reduces considerably the spectral resolution required to isolate emissions of interest. Thus, the spectral detection system can be simple and compact. For many metals, a simple interference filter/photomultiplier tube combination suffices for the detection system.

A more recent implementation of spark spectroscopy uses a laser-generated spark to breakdown air and excite emissions from species within the spark. This approach has two significant limitations. Laser-produced sparks are quite small, having dimensions on the order of tens of microns. In addition, energies for compact, portable lasers are relatively small, roughly 10 to 100 mJ. These drawbacks mean a laser-based system will have a relatively cool excitation plasma and small sample volume. The cooler excitation plasma results in reduced brightness of spectral emissions, while the small excitation volume results in very large spark-to-spark variations in emission intensities. Both of these liabilities severely limit the ultimate sensitivity achievable by compact laser-spark systems.

Our system, on the other hand, produces a plasma with a 1 to 5 J spark which fills a volume with dimensions of several millimeters. These two advantages result in our ability to achieve sensitivities at parts per billion levels, whereas laser-spark systems generally are limited to sensitivities of 10 to 100 parts per million, more than three orders of magnitude worse. Use of a large laser would alleviate some of these problems, but then the system would become impossibly complex and expensive.

## Results

### Technology Extension

**Experimental details of SIBS measurements.** Our apparatus for developing the SIBS technology has three major sections (Figure 3), an aerosol generator, a spark excitation system, and a detection system. The aerosol generator has two components: a droplet generator and a drying column. The aerosols are created by first making small droplets of precisely defined

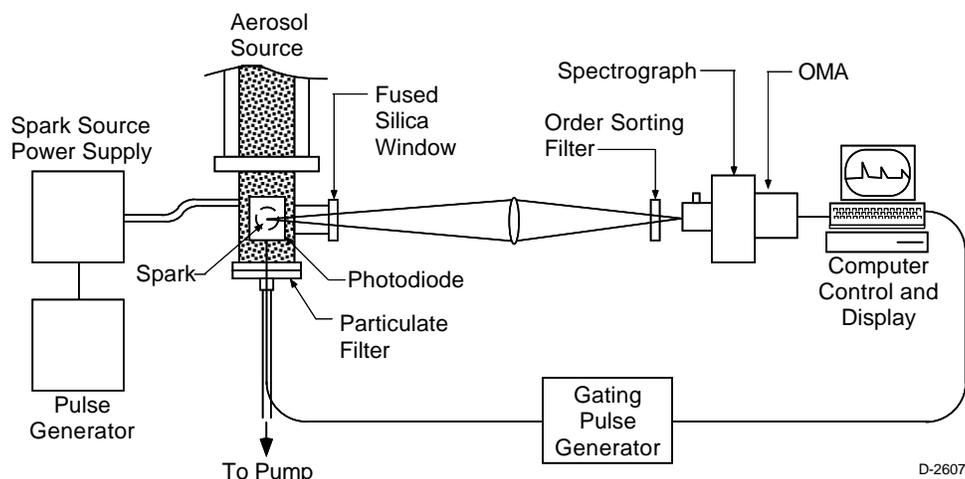


Figure 3. Schematic of system for detecting contaminants on particles or aerosols using the SIBS technique.

characteristics from an aqueous solution of the analyte species, and then driving off the water from these droplets so that only dry particulate remains. This system is described in more detail below.

The spark chamber resides at the bottom of the drying column and houses the electrodes. The electrodes are mounted directly to stainless steel blocks which are in turn mounted on ceramic standoffs inserted into the sealed aerosol source. The chamber has arms with windows at the ends to pass the emission generated upon sparking. The detection system (monochromator and OMA, or interference filter and photomultiplier tube) is specifically designed to eliminate interference from the prompt spark-plasma emission.

Our spark-generating power supply produces volume-filling 5 J sparks at varying repetition rates from single shot to >20 Hz. It is driven by a delay generator that allows the sparks to occur at set intervals. Because of the possibility of the occasional misfire or delayed sparking event, the detection system is triggered by a photodiode. When the radiation from the spark is observed by the photodiode, a second delay generator is activated. This generator delays the turn-on time of the OMA, so that it will not be saturated by the very bright initial plasma of the spark itself. This initial bright emission is dominated by a spectral continuum arising from free electrons (bremsstrahlung radiation) present in the spark-created plasma.

**Aerosol Generator Calibration System.** As mentioned, the aerosol generator has two components: a droplet generator and a drying column. The droplet generator is a variant on the design first demonstrated by Berglund and Liu<sup>2</sup> and is shown in Figure 4. The operating principle involves the imposition of a periodic instability on a thin stream of fluid flowing from a pinhole orifice. The instability is induced by coupling a single frequency vibration into the fluid using a piezoelectric transducer driven by a square wave function generator. Under certain conditions of fluid flow rate and instability frequency, monodisperse aerosols are generated.

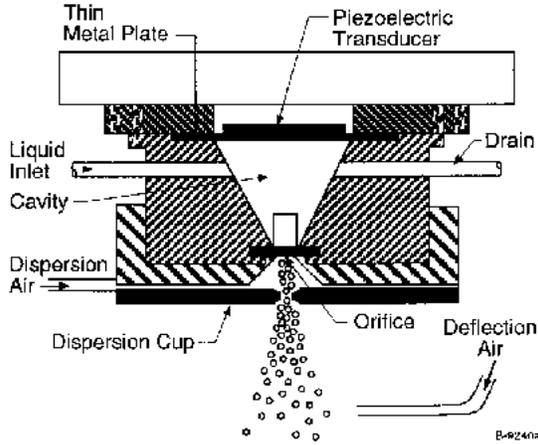


Figure 4. The monodisperse droplet generator.

The size of the droplet is a function of the instability frequency and fluid flow rate through the orifice:

$$D_p = \left( \frac{6Q}{\pi f} \right)^{\frac{1}{3}} \quad (1)$$

in which Q is the fluid flow rate and f is the frequency. The fluid flow rate is itself a function of orifice size. Typically we use 20 μm diameter orifices which result in a flow rate of 0.34 ml min<sup>-1</sup>. For this flow rate and a generation frequency of 100 kHz, this system produces 48 μm diameter droplets.

This droplet generator is situated at the top of a Plexiglas tube in a downward directed orientation toward the drying column (Figure 5). Loss of particles in the drying column walls is minimized by the use of a porous stainless steel inner tube through which air is drawn at a fixed rate. The air is heated to 100°C to facilitate removal of water from the droplets and is drawn out the bottom of the column by a filtered pumping system. The dry aerosol is trapped on a filter placed at the bottom of a Plexiglas extension under the drying column that houses the spark chamber. This filter prevents particles from exiting the generator and contaminating the laboratory environment.

In order to calculate the concentration of aerosol in the air, one needs to measure the efficiency with which the aerosol traverses the drying tube:

$$C_{\text{ppmw(air)}} = \frac{M(\text{gm/min}) \cdot E}{F(\text{cm}^3/\text{min}) \cdot \rho(\text{gm/cm}^3)} 1 \times 10^6 \quad (2)$$

Here, M is the mass introduction rate, E is the passage efficiency (particle loss in the generator), F is the air flow rate and ρ is the air density. Under normal operating conditions in the generator, a 1% by weight solution of lead nitrate corresponds to about 50 ppmw (Pb in air). The only component of this equation that is related to the initial concentration of lead is

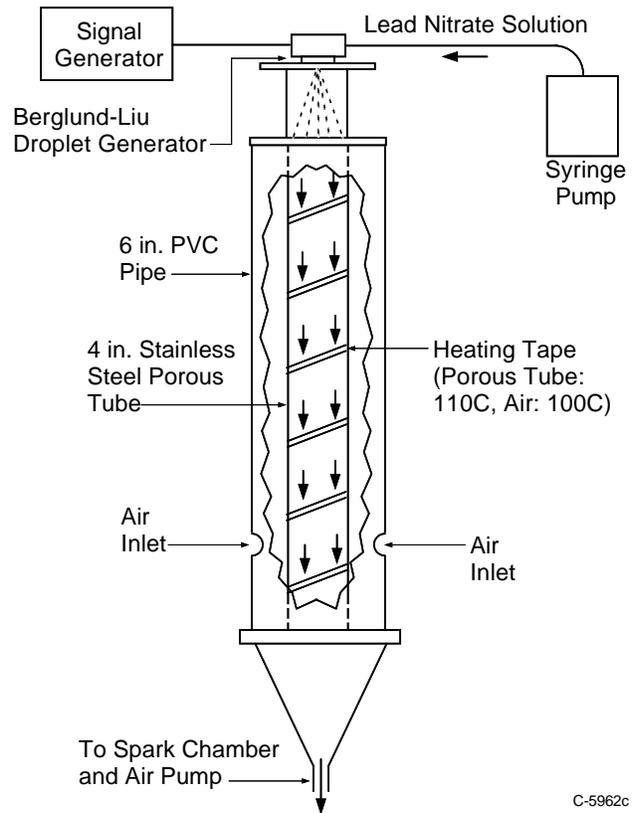


Figure 5. The dry aerosol source, including spark chamber and drying tube.

the mass introduction rate. Therefore, to calibrate for other densities, different solution concentrations need to be introduced.

When the dry aerosol is exposed to the spark, it is atomized and excited simultaneously. To avoid errors associated with inhomogeneity in sampling, having a volume-filling spark that samples many particles at once is desirable. Our aerosol source produces sufficient particle densities to ensure the processing of many particles during a spark event:

$$\rho(\text{cm}^{-3}) = \frac{R(\text{s}^{-1}) \cdot E}{F(\text{cm}^3 \text{s}^{-1})}, \quad (3)$$

where R is the particle generation rate (100 kHz), E is the passage efficiency, and F is the gas flow rate through the system. In a typical experiment, the particle density is about  $170 \text{ cm}^{-3}$ . A 5 J spark transcribes a cylinder that is 7 mm in length and 4 mm in diameter. The corresponding volume is  $0.09 \text{ cm}^3$ . Consequently, about 16 aerosol particles were sampled in each pulse. Naturally, sampling many particles not only results in reduced sample inhomogeneity errors, but also in larger signal levels.

We calibrated the dry aerosol generator gravimetrically by comparing the mass rate at which solute passes through the particle generator with the mass recovered on the filter at the bottom of the drying tube. This establishes the efficiency at which particles pass through the apparatus. As shown in Table 1, which compares the results of mass recoveries with corresponding calculations of dry particle diameter and concentration for lead, our mass recoveries are uniformly high (0.85 to 0.95), indicating that particle losses within the generator/drying tube are minimal.

Table 1. Typical Results from Lead-Aerosol Mass Recovery Tests

Solution Concentration (% wt)	Mass Recovery Efficiency	Dry Particle Diameter (microns)	Lead Concentration (ppmw in air)
0.091	0.95	4.6	8.6
0.41	0.9	7.6	36.2
0.41	0.88	7.6	35.8
0.93	0.85	10	78.4

**SIBS Spectra of Aerosols.** Figure 6 shows the spectra of lead nitrate aerosols, at several different concentrations, near 405.8 nm. Data similar to those in Figure 6 taken for a number of different aerosol concentrations allows construction of a calibration curve (Figure 7). The minimum detection limit (MDL) deduced from this curve 10 ppbw or  $12 \mu\text{g m}^{-3}$ , well below the NIOSH TWA limit for lead dust (80 ppbw or  $0.10 \text{ mg m}^{-3}$ ).

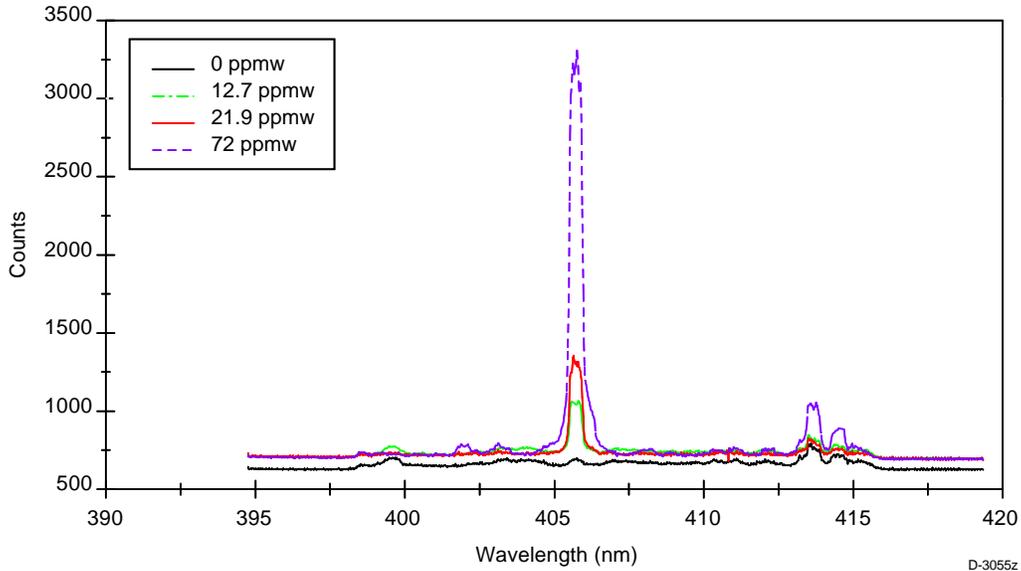


Figure 6. SIBS spectra around 406 nm at different Pb-aerosol concentrations.

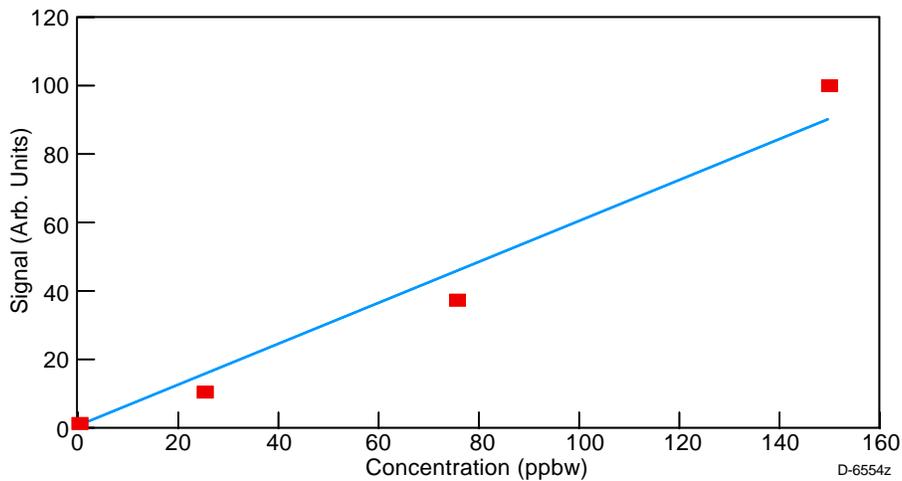


Figure 7. Calibration curve for the detection of Pb aerosols by SIBS.

Figures 8 and 9 show representative SIBS spectra and the accompanying calibration curve for uranium detection. Table 2 summarizes the results for a number of species investigated. Because we were intent on surveying many different species, we did not spend much time optimizing detection of individual species. We are confident that with a little refinement in our detection and analysis techniques that the MDLs given in Table 2 can be reduced significantly. As it stands, our MDLs are already significantly below the proposed regulatory limits for most species.

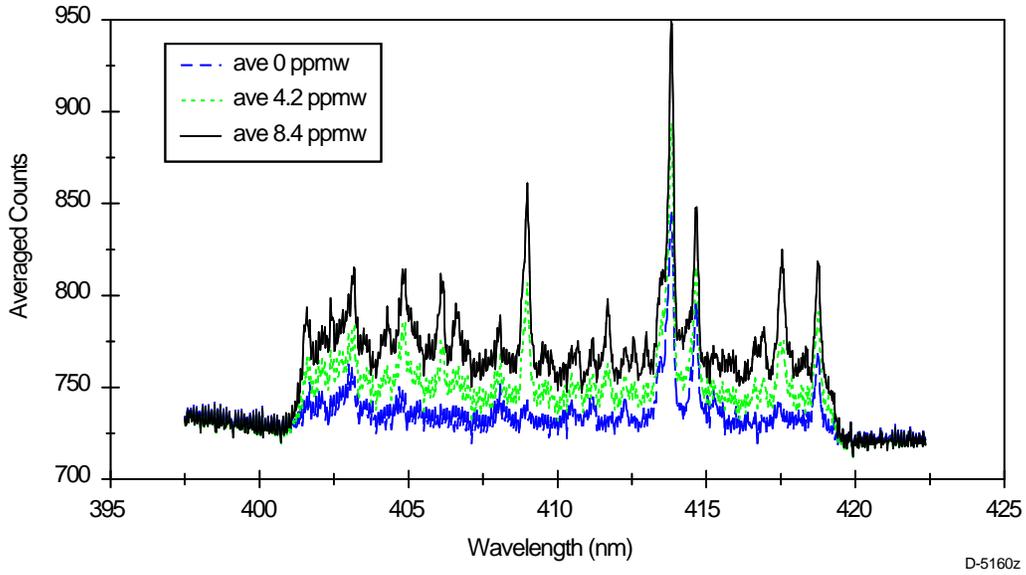


Figure 8. SIBS spectra around 410 nm for several different U-aerosol concentrations.

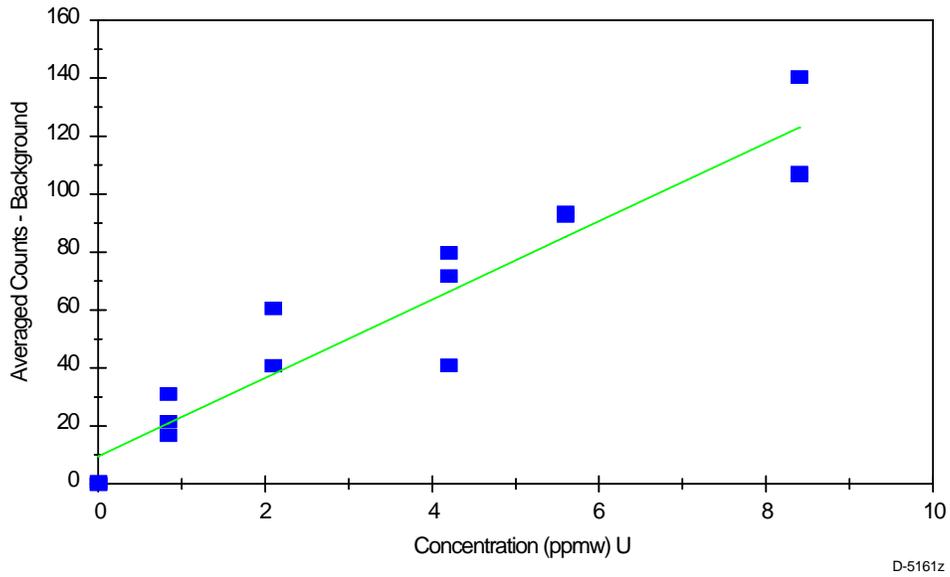


Figure 9. Calibration curve for the detection of U-containing aerosols by SIBS.

Table 2. SIBS Detection Sensitivities

Element	Detection Sensitivity (ppbw)	Regulatory Limit (ppbw)
Pb	10	40
Hg	<25	40
Cd	<100	80
Cr	<10	400
U	<300	500
Th	<1000	120
Mn (Tc)	<40	-2.5

### Identification of Near-Term Applications

We have identified several applications where our technology can address DOE needs in the near term:

- Off-gas continuous emissions monitoring
  - vitrification plants
  - hazardous waste incineration
- Process control for vitrification or incineration
- Ambient air quality during decontamination and dismantlement processes
- Monitoring/controlling decontamination procedures
  - Pb-based paint removal
  - cement-floor scabbling.

We are currently in the process of extending our technology to water-quality monitoring.

The items on this list have the common feature that the contamination to be measured is air-borne. The compact nature of our sampling head, and the relatively inert nature of the materials used in its fabrication, allow off-gas monitoring to be done *in situ*. That is, the samples need not be removed from the flue through a probe first. One can verify contamination levels, in real time, because our monitor provides readings every few minutes at the most. Thus, one can ensure that RCRA metals and species such as U and Th remain below proposed regulatory limits. Furthermore, because our detection is real time, species concentration measurements can be used for process control purposes. That is feed rates of hazardous materials, or additives used

in off-gas cleanup processes can be varied in real time to make the processes work at their most efficient levels.

While most decontamination and dismantlement processes are designed to minimize the escape of contaminated dust, no containment process is completely fool proof. In addition, it may be possible in some situations to relax containment procedures considerably without adversely affecting worker safety. Our system could be placed on location, where the clean up processes are being undertaken, to ensure that ambient air quality remains below levels that pose a hazard to workers. As we understand it, current procedure involves considerable over application of safety measures just to be safe. This over application can be both expensive and inefficient. Employing one of our stand-alone systems on site could result in considerable speed up of remediation operations without compromising worker safety.

Finally, a number of decontamination processes involve activities in which coatings are removed from surfaces, or thin layers of the surfaces themselves are removed. In particular, DOE sites are reputed to contain thousands of acres of concrete that is contaminated by various materials such as uranium and thorium. Our monitor could be used in concert with the decontamination processes to signal when the coatings were completely removed, or when a contaminated floor had been scabbled to sufficient depth that remaining contaminant levels were no longer a hazardous.

### **Engineering Design of Prototype Instrument**

Physical Sciences Inc's SIBS-based hazardous waste monitor has four essential components:

1. A spark system for atomizing the aerosols and exciting contaminant fluorescence;
2. A detection system for separating contaminant fluorescence from other features excited by the spark;
3. A data processing system for controlling the various instrument components, for collecting the data, for converting the raw data into hazardous waste concentrations in the sample, and for reporting and archiving hazardous waste analysis results; and
4. A calibration system to ensure the accuracy of the hazardous waste measurement.

Figure 10 shows a block schematic of the instrument with component subsystems identified. A small pump draws samples through the spark chamber where any aerosols are vaporized and contaminant fluorescence is excited. Optical fibers collect light from the spark region and transport it to the detection module. This module is either a pair of matched photometers for single element detection, or an optical multichannel analyzer (OMA) for multielement detection. The detected signals are read and processed by a computer system, and results are displayed and stored. The computer system also provides timing signals to drive the spark

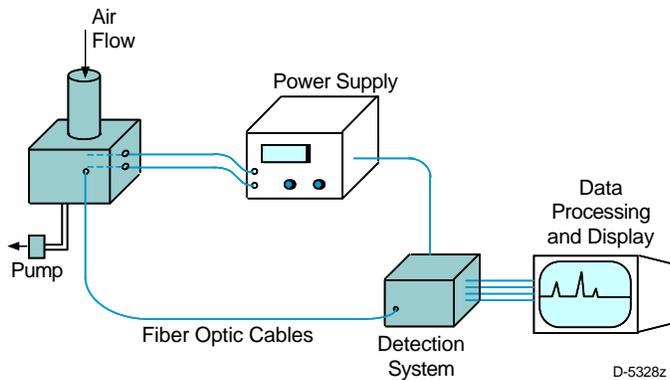


Figure 10. Block diagram of SIBS-based hazardous waste monitor.

source and gate the detection system, and where needed, can also provide feedback signals for active control of remediation processes.

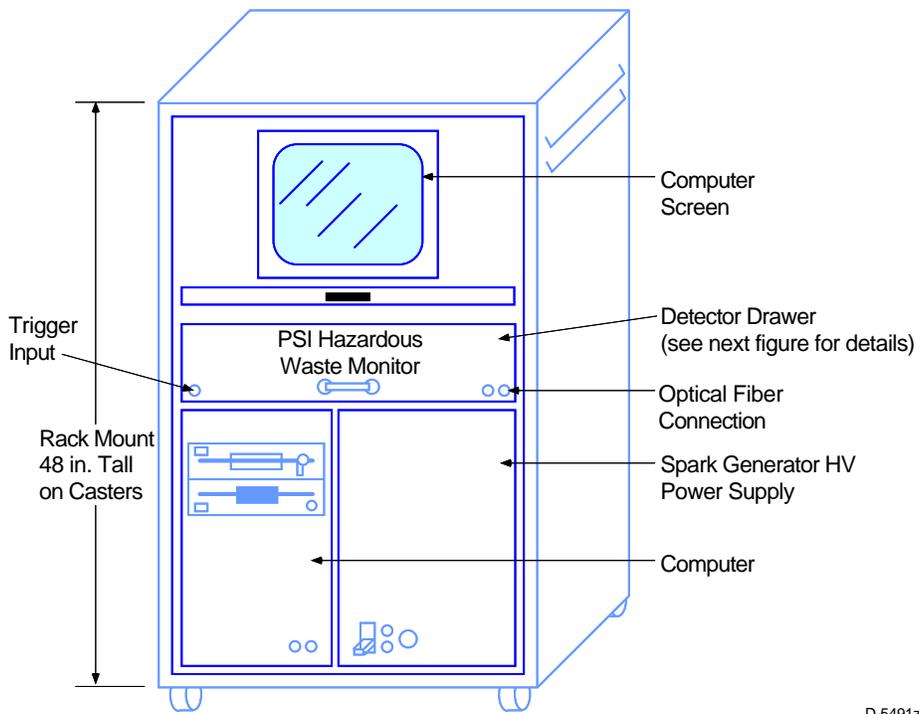
A calibration system is included with the instrument. This system generates known quantities of contaminant, and is so configured that the detection head can be bolted directly to it.

Our system performance and design specifications are as follows:

- Ability to detect heavy metals and radionuclides in gas phase and on particulates
- Sensitivity range for all species below OSHA limits
- Calibration for all contaminant species
- Analysis and display of results in less than 1 min
- Size, <math><65 \times 65 \times 125 \text{ cm}</math> ( $\approx 15 \text{ ft}^3$ )
- Weight <math><115 \text{ kg}</math>
- Power <math><3.5 \text{ kW}</math>

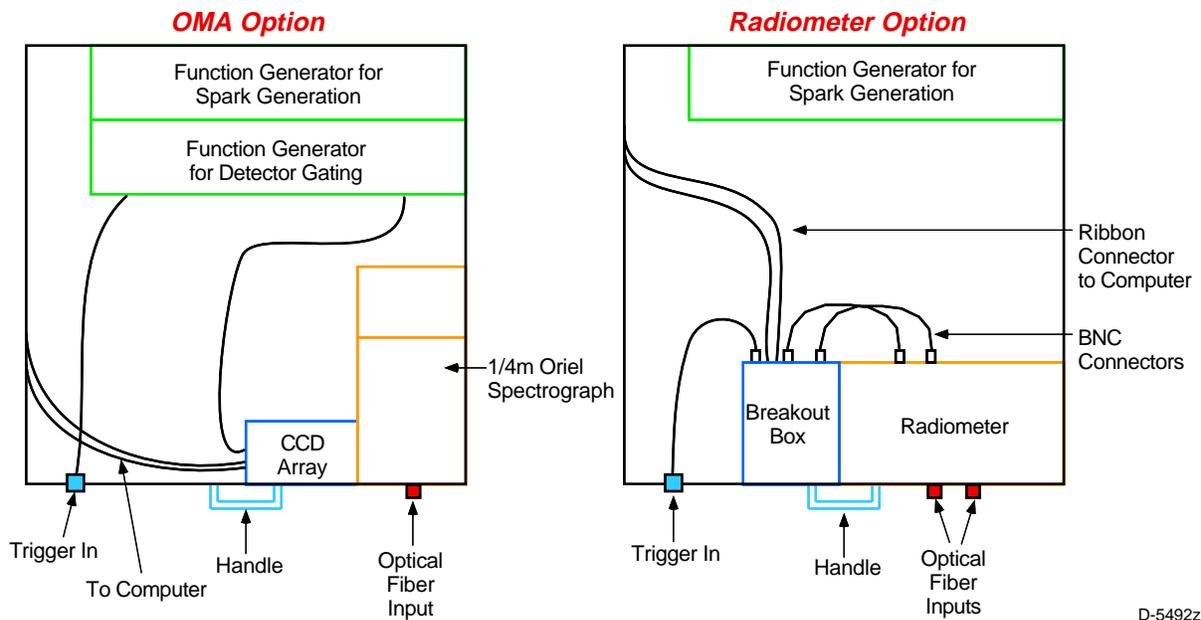
The system components of the Hazardous Waste Monitor are arranged as indicated in Figures 11 and 12. The timing and triggering electronics, the discharge power supply, the spectral dispersion and detection module, and the data acquisition and control system are contained in a standard, half-height 19 in. equipment rack. The sensor head containing the electrodes and fiber optic collection optics is contained in a separate, small portable module. The sensor head connects to the main instrument via an umbilical containing the optical fibers and the cables to power the spark system. This arrangement allows ready placement of the sensor head at desired locations, including those remote from the main system. The system requires standard 115 VAC power.

We currently have under testing prototype SIBS-based Pb and Cr monitors we developed using internal funding. These are the units we demonstrated recently at the CEMs tests at Research Triangle Park. The details of these tests should be available shortly.



D-5491z

Figure 11. Diagram of complete hazardous waste monitor.



D-5492z

Figure 12. Details of the detector system drawers. In one case when an OMA is needed as the detector; in the other when a filtered photometer suffices for detection.

## Conclusions

During the second phase of the program we demonstrated sensitive detection of a number of species, both RCRA metals (Sb, Be, Cd, Cr, Pb, As, Hg) and radionuclides (U, Th, Mn -- a Tc surrogate). In general, detection was achieved in real time with sensitivities at levels of parts-per-billion by weight (ppbw) and linear dynamic ranges (LDRs) in excess of  $10^3$ . We identified several near-term applications for our technology which would benefit D&D operations, including, monitoring and control of decontamination procedures such as coatings removal or floor scrubbing processes, ambient air quality during decontamination and dismantlement processes, off-gas continuous emissions monitoring and process control of vitrification or incineration facilities. We plan soon to expand this list to include water-quality monitoring. In addition, we designed a prototype instrument. This instrument will be fabricated and tested, both in the laboratory and the field during the program's third phase.

The baseline technology for toxic metal detection is sample collection followed by laboratory analysis. Lab testing is highly reliable and accurate, but has the drawback of long response times, typically three to four weeks. In addition sample collection, logging, transportation, and lab fees are a significant cost item on many clean-up projects. Both labor and analysis costs could be reduced significantly, therefore, if portable, real-time field analysis instruments become available.

We think that the SIBS technology has significant advantages over competing technologies in providing such capabilities. Figure 13 shows schematically the relative costs and sensitivities of a number of competing technologies that can be incorporated into field instruments and continuous emissions monitors. SIBS-based instruments provide significant cost and/or sensitivity advantages over them all.

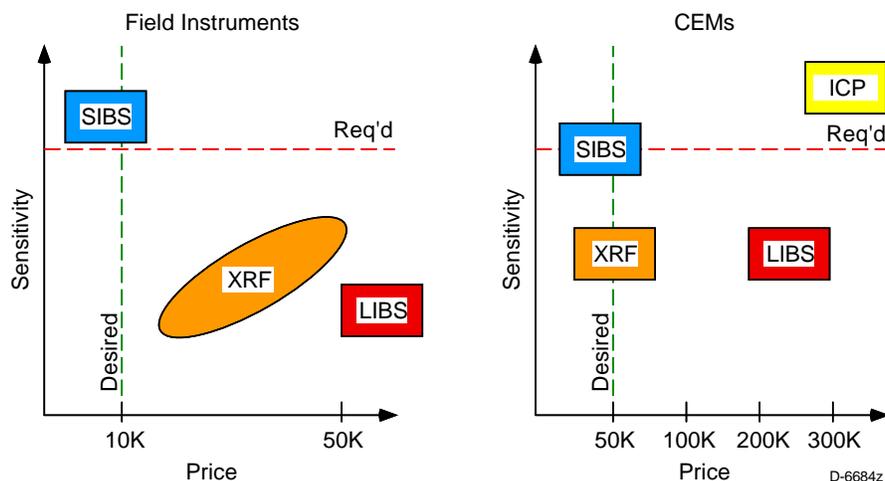


Figure 13. Schematic representation of relative costs of SIBS-based instruments and those of competitive technologies.

We have begun commercialization activities to enable technology transfer to the commercial sector. This includes drawing up a business plan, participation in DOE's Dawn-breaker program, and preliminary discussions with potential commercial partners.

## Acknowledgments

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